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<b>(21) International Application Number:</b> PCT/US90/06360 <b>(22) International Filing Date:</b> 1 November 1990 (01.11.90)  <b>(30) Priority data:</b> 432,259 6 November 1989 (06.11.89) US  <b>(71) Applicant:</b> ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).  <b>(72) Inventors:</b> LI, Hsin, Lang ; 3 Fernwood Place, Parsippany, NJ 07054 (US). LIN, Leroy, Chi-Tsun ; 3742 Harvette Drive, Richmond, VA 23234 (US). PREVORSEK, Dusan, Ciril ; 21 Harwich Road, Morristown, NJ 07960 (US). CHIN, Hong, Bai ; 16 Hidden Glen Drive, Parsippany, NJ 07054 (US).		<b>(74) Agent:</b> ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C. A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> BALLISTIC RESISTANT COMPOSITE ARTICLE HAVING IMPROVED MATRIX SYSTEM  <b>(57) Abstract</b>  An impact resistant rigid composite article comprising a fibrous layer comprising a network of filaments dispersed in a rigid matrix comprising one or more thermosetting resins and one or more thermoplastic resins.		

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BALLISTIC RESISTANT COMPOSITE  
ARTICLE HAVING IMPROVED MATRIX SYSTEM

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Background of the Invention

1. Field of the Invention

This invention relates to ballistic resistant  
10 composite articles. More particularly, this invention  
relates to such articles having improved ballistic  
protection.

2. Prior Art

15 Ballistic articles such as bulletproof vests,  
helmets, structural members of helicopters and other  
military equipment, vehicle panels, briefcases,  
raincoats and umbrellas containing high strength  
fibers are known. Fibers conventionally used include  
20 aramid fibers such as poly(phenylenediamine  
terephthalamide), graphite fibers, nylon fibers,  
ceramic fibers, glass fibers and the like. For many  
applications, such as vests or parts of vests, the  
fibers are used in a woven or knitted fabric. For  
25 many of the applications, the fibers are encapsulated  
or embedded in a matrix material.

In "The Application of High Modulus Fibers to  
Ballistic Protection", R.C. Laible et al., J.  
Macromol. Sci.-Chem., A7(1), pp. 295-322, 1973, it is  
30 indicated on p. 298 that a fourth requirement is that  
the textile material have a high degree of heat  
resistance. In an NTIS publication, AD-A018 958 "New  
Materials in Construction for Improved Helmets", A.L.  
Alesi et al., a multilayer highly oriented  
35 polypropylene film material (without matrix), referred  
to as "XP", was evaluated against an aramid fiber  
(with a phenolic/polyvinyl butyral resin matrix). The  
aramid system was judged to have the most promising

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combination of superior performance and a minimum of problems for combat helmet development. USP 4,403,012 and USP 4,457,985 disclose ballistic resistant composite articles comprised of networks of high molecular weight polyethylene or polypropylene fibers, and matrices composed of olefin polymers and copolymers, unsaturated polyester resins, epoxy resins, and other resins curable below the melting point of the fiber.

10 A.L. Lastnik, et al., "The Effect of Resin Concentration and Laminating Pressures on KEVLAR Fabric Bonded with Modified Phenolic Resin", Tech. Report NATICK/TR-84/030, June 8, 1984; disclose that an interstitial resin, which encapsulates and bonds  
15 the fibers of a fabric, reduces the ballistic resistance of the resultant composite article.

US Patent Nos. 4,623,574 and 4,748,064 disclose a simple composite structure comprising high strength fibers embedded in an elastomeric matrix. The simple  
20 composite structure exhibits outstanding ballistic protection as compared to simple composites utilizing rigid matrices, the results of which are disclosed in the patents. Particularly effective are simple composites employing ultra-high molecular weight  
25 polyethylene and polypropylene such as disclosed in US Patent No. 4,413,110.

US Patent Nos. 4,737,402 and 4,613,535 disclose complex rigid composite articles having improved impact resistance which comprise a network of high  
30 strength fibers such as the ultra-high molecular weight polyethylene and polypropylene disclosed in US Patent No. 4,413,110 embedded in an elastomeric matrix material and at least one additional rigid layer on a major surface of the fibers in the matrix. It is  
35 disclosed that the composites have improved resistance to environmental hazards, improved impact resistance and are unexpectedly effective as ballistic resistant

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articles such as armor.

#### SUMMARY OF THE INVENTION

One aspect of the present invention relates to a  
5 ballistic-resistant rigid composite comprised of one or  
more layers, at least one of said layers is a fibrous  
layer comprising a network of high strength filaments  
having a tenacity of at least about 7 grams/denier, a  
tensile modulus of at least about 160 grams/denier and an  
10 energy-to-break of at least about 8 joules/gram in a rigid  
matrix material, wherein said matrix material comprising  
one or more thermoplastic polymers and one or more  
thermosetting resin. The composites of this invention  
exhibit good handling characteristics and long shelf life  
15 and resist delamination due to impact. During the molding  
of the composites of this invention, no or substantially  
no mold cooling is required, and mold cycle times are  
short, preferably less than about 30 minutes.

#### DETAILED DESCRIPTION OF THE INVENTION

20 Composites of this invention comprise a network of  
filaments in a rigid matrix which comprises one or more  
thermoplastic polymers and one or more thermosetting  
25 resins.

The cross-section of filaments for use in this  
invention may vary widely. Useful filaments may have a  
circular cross-section, oblong cross-section or irregular  
or regular multi-lobal cross-section having one or more  
30 regular or irregular lobes projecting from the linear or  
longitudinal axis of the filament. In the particularly  
preferred embodiments of the invention, the filaments are  
of substantially circular or oblong cross-section and in  
the most preferred embodiments are of circular or  
35 substantially circular cross-section.

In the composite articles of this invention, the  
filaments may be arranged in networks having various

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configurations. For example, a plurality of filaments can be grouped together to form twisted or untwisted yarnbundles in various alignments. The filaments or yarn may be formed as a felt, knitted or woven (plain, basket, 5 satin and crow feet weaves, etc.) into a network, fabricated into non-woven fabric, arranged in parallel array, layered, or formed into a woven fabric by any of a variety of conventional techniques. Among these techniques, for ballistic resistance applications we 10 prefer to use those variations commonly employed in the preparation of aramid fabrics for ballistic-resistant articles. For example, the techniques described in U.S. Patent No. 4,181,768 and in M.R. Silyquist et al., J. Macromol Sci. Chem., A7(1), pp. 203 et. seq. (1973) are 15 particularly suitable. In preferred embodiments of the invention, the filaments in each layer are aligned in a substantially parallel and unidirectional fashion, and the matrix material substantially coats the individual filaments.

20 The type of filaments used in the fabrication of the article of this invention may vary widely and can be metallic filaments, semi-metallic filaments, inorganic filaments and/or organic filaments. Preferred filaments for use in the practice of this invention are those having 25 a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 150 g/d and an energy-in-break equal to or greater than about 8 joules/gram. Particularly preferred filaments are those having a tenacity equal to or greater than about 20 g/d, a 30 tensile modulus equal to or greater than about 500 g/d and energy-in-break equal to or greater than about 30 joules/grams. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the tenacity of the filaments are equal to or greater than 35 about 25 g/d, the tensile modulus is equal to or greater than about 1000 g/d, and the energy-to-break is equal to or greater than about 35 joules/grams. In the practice of

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this invention, filaments of choice have a tenacity equal to or greater than about 30 g/d, the tensile modulus is equal to or greater than about 1300 g/d and the energy-to-break is equal to or greater than about 40  
5 joules/grams.

Filaments for use in the practice of this invention may be metallic, semi-metallic, inorganic and/or organic. Illustrative of useful inorganic filaments are those formed from S-glass, silicon carbide, asbestos, basalt,  
10 E-glass, alumina, alumina-silicate, quartz, zirconia-silica, ceramic filaments, boron filaments, carbon filaments, and the like. Exemplary of useful metallic or semi-metallic filaments are those composed of boron, aluminum, steel and titanium. Illustrative of  
15 useful organic filaments are those composed of aramids (aromatic polyamides), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2,2,2-trimethyl-hexamethylene terephthalamide), poly(piperazine sebacamide), poly(metaphenylene isophthalamide) (Nomex)  
20 and poly(p-phenylene terephthalamide) (Kevlar) and aliphatic and cycloaliphatic polyamides, such as the copolyamide of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, the copolyamide of up to 30% bis-(-amidocyclohexyl) methylene,  
25 terephthalic acid and caprolactam, polyhexamethylene adipamide (nylon 66), poly(butyrolactam) (nylon 4), poly(9-aminonanoic acid) nylon 9), poly(ε-antholactam) (nylon 7), poly(ε-caprolactam) (nylon 8), polycaprolactam (nylon 6), poly(p-phenylene terephthalamide),  
30 polyhexamethylene sebacamide (nylon 6,10), polyaminoundecanamide (nylon 11), polydodecanolactam (nylon 12), polyhexamethylene isophthalamide, polyhexamethylene terephthalamide, polycaproamide, poly(nonamethylene azelamide) (Nylon 9,9),  
35 poly(decamethylene azelamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis-4-aminocyclohexyl)methane 1,10-decanedi-

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- carboxamide](Qiana)(trans), or combination thereof; and aliphatic, cycloaliphatic and aromatic polyesters such as poly(1,4-cyclohexylidene dimethyl eneterephthalate) cis and trans, poly(ethylene-2,6-naphthalate),
- 5 poly(1,4-cyclohexane dimethylene terephthalate) (trans), poly(decamethylene terephthalate, poly(ethylene terephthalate), poly(ethylene isophthalate), poly(ethylene oxybenzoate), poly(para-hydroxy benzoate), poly( , dimethylpropiolactone), poly(decamethylene adipate),
- 10 poly(ethylene succinate) and the like.

Also illustrative of useful organic filaments are those composed of extended chain polymers formed by polymerization of ,  $\beta$ -unsaturated monomers of the formula:



wherein:

- $R_1$  and  $R_2$  are the same or different and are hydrogen, hydroxy, halogen, alkylcarbonyl, carboxy, alkoxy, carbonyl, heterocycle or alkyl or aryl either unsubstituted or
- 20 substituted with one or more substituents selected from the group consisting of alkoxy, cyano, hydroxy, alkyl and aryl. Illustrative of such polymers of ,  $\beta$ -unsaturated monomers are polymers including polystyrene, polyethylene,
- 25 polypropylene, poly(1-octadecene), polyisobutylene, poly(1-pentene), poly(2-methylstyrene), poly(4-methylstyrene), poly(1-hexene), poly(1-pentene), poly(4-methoxystyrene), poly(5-methyl-1-hexene), poly(4-methylpentene), poly(1-butene), poly(3-
- 30 methyl-1-butene), poly(3-phenyl-1-propene), polyvinyl chloride, polybutylene, polyacrylonitrile, poly(methyl pentene-1), poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl butyral), poly(vinyl chloride), poly(vinylidene chloride), vinyl chloride-vinyl acetate chloride
- 35 copolymer, poly(vinylidene fluoride), poly(methyl acrylate, poly(methyl methacrylate), poly(methacrylonitrile), poly(acrylamide), poly(vinyl fluoride),



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poly(vinyl formal), poly(3-methyl-1-butene), poly(1-pentene), poly(4-methyl-1-butene), poly(1-pentene), poly(4-methyl-1-pentene), poly(1-hexane), poly(5-methyl-1-hexene), poly(1-octadecene), poly(vinyl cyclopentane),  
5 poly(vinylcyclohexane),  
poly(a-vinylnaphthalene), poly(vinyl methyl ether),  
poly(vinylethylether), poly(vinyl propylether), poly(vinyl carbazole), poly(vinyl pyrrolidone),  
poly(2-chlorostyrene), poly(4-chloro-  
10 styrene), poly(vinyl formate), poly(vinyl butyl ether),  
poly(vinyl octyl ether), poly(vinyl methyl ketone),  
poly(methylisopropenyl ketone), poly(4-phenylstyrene) and  
the like.

In the most preferred embodiments of the invention,  
15 composite articles include a filament network, which may  
include a high molecular weight polyethylene filament, a  
high molecular weight polypropylene filament, an aramid  
filament, a high molecular weight polyvinyl alcohol  
filament, a high molecular weight polyacrylonitrile  
20 filament or mixtures thereof. USP 4,457,985 generally  
discusses such high molecular weight polyethylene and  
polypropylene filaments, and the disclosure of this patent  
is hereby incorporated by reference to the extent that it  
is not inconsistent herewith. In the case of  
25 polyethylene, suitable filaments are those of molecular  
weight of at least 150,000, preferably at least one  
million and more preferably between two million and five  
million. Such extended chain polyethylene (ECPE)  
filaments may be grown in solution as described in U.S.  
30 Patent No. 4,137,394 to Meihuizen et al., or U.S. Patent  
No. 4,356,138 of Kavesh et al., issued October 26, 1982,  
or a filament spun from a solution to form a gel  
structure, as described in German Off. 3,004,699 and GB  
2051667, and especially described in Application Serial  
35 No. 572,607 of Kavesh et al., filed January 20, 1984 (see  
EPA 64,167, published Nov. 10, 1982). As used herein, the  
term polyethylene shall mean a predominantly linear

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polyethylene material that may contain minor amounts of chain branching or comonomers not exceeding 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 wt% of one or more polymeric additives such as alkene-1-polymers, in particular low density polyethylene, polypropylene or polybutylene, copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as anti-oxidants, lubricants, ultra-violet screening agents, colorants and the like which are commonly incorporated by reference. Depending upon the formation technique, the draw ratio and temperatures, and other conditions, a variety of properties can be imparted to these filaments. The tenacity of the filaments should be at least 15 grams/denier, preferably at least 20 grams/denier, more preferably at least 25 grams/denier and most preferably at least 30 grams/denier. Similarly, the tensile modulus of the filaments, as measured by an Instron tensile testing machine, is at least 300 grams/denier, preferably at least 500 grams/denier and more preferably at least 1,000 grams/denier and most preferably at least 1,200 grams/denier. These highest values for tensile modulus and tenacity are generally obtainable only by employing solution grown or gel filament processes.

Similarly, highly oriented polypropylene filaments of molecular weight at least 200,000, preferably at least one million and more preferably at least two million may be used. Such high molecular weight polypropylene may be formed into reasonably well oriented filaments by the techniques prescribed in the various references referred to above, and especially by the technique of U.S. Serial No. 572,607, filed January 20, 1984, of Kavesh et al. and commonly assigned. Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with

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polypropylene are generally substantially lower than the corresponding values for polyethylene. Accordingly, a suitable tenacity is at least 8 grams/denier, with a preferred tenacity being at least 11 grams/denier. The tensile modulus for polypropylene is at least 160 grams/denier, preferably at least 200 grams/denier. The particularly preferred ranges for the above-described parameters can advantageously provide improved performance in the final article.

10 High molecular weight polyvinyl alcohol filaments having high tensile modulus are described in USP 4,440,711 to Y. Kwon et al., which is hereby incorporated by reference to the extent it is not inconsistent herewith. In the case of polyvinyl alcohol (PV-OH), PV-OH filament  
15 of molecular weight of at least about 200,000. Particularly useful PV-OH filament should have a modulus of at least about 300 g/d, a tenacity of at least 7 g/d (preferably at least about 10 g/d, more preferably at about 14 g/d, and most preferably at least about 17 g/d),  
20 and an energy-to-break of at least about 8 joules/gram. PV-OH filaments having a weight average molecular weight of at least about 200,000, a tenacity of at least about 10 g/d, a modulus of at least about 300 g/d, and an energy-to-break of about 8 joules/gram are more useful in  
25 producing a ballistic resistant article. PV-OH filament having such properties can be produced, for example, by the process disclosed in U.S. Patent No. 4,599,267.

In the case of polyacrylonitrile (PAN), PAN filament of molecular weight of at least about 400,000.  
30 Particularly useful PAN filament should have a tenacity of at least about 10 g/d and an energy-to-break of at least about 8 joules/gram. PAN filament having a molecular weight of at least about 400,000, a tenacity of at least about 15 to about 20 g/d and an energy-to-break of at  
35 least 8 joules/gram is most useful in producing ballistic resistant articles; and such filaments are disclosed, for example, in U.S. 4,535,027.

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In the case of aramid filaments, suitable aramide filaments formed principally from aromatic polyamide are described in USP 3,671,542, which is hereby incorporated by reference. Preferred aramid filament will have a  
5 tenacity of at least about 20 g/d, a tensile modulus of at least about 400 g/d and an energy-to-break at least about 8 joules/gram, and particularly preferred aramid filaments will have a tenacity of at least about 20 g/d, a modulus  
10 of at least about 480 g/d and an energy-to-break of at least about 20 joules/gram. Most preferred aramid filaments will have a tenacity of at least about 20 g/denier, a modulus of at least about 900 g/denier and an energy-to-break of at least about 30 joules/gram. For example, poly(phenylenediamine terephthalamide) filaments  
15 produced commercially by Dupont Corporation under the trade name of Kevlar 29, 49, 129 and 149 having moderately high moduli and tenacity values are particularly useful in forming ballistic resistant composites. Also useful in the practice of this invention  
20 is poly(metaphenylene isophthalamide) filaments produced commercially by Dupont under the tradename Nomex.

The filaments are dispersed in a continuous phase of a rigid matrix material which preferably substantially coats each filament contained in the bundle of filament.  
25 The manner in which the filaments are dispersed may vary widely. The filaments may be aligned in a substantially parallel, unidirectional fashion, or filaments may be aligned in a multidirectional fashion with filaments at varying angles with each other. In the preferred  
30 embodiments of this invention, filaments in each layer are aligned in a substantially parallel, unidirectional fashion such as in a prepreg, pultruded sheet and the like.

The matrix material employed in the practice of this invention comprises one or more thermosetting resins and  
35 one or more thermoplastic resins, preferably as a blend of such resins. As used herein "thermoplastic resins" are resins which can be heated and softened, cooled and

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hardened limitless times without undergoing a basic alteration, and "thermosetting resins" are resins which do not tolerate thermal cycling and which cannot be resoftened and reworked after molding, extruding or casting and which attain new, irreversible properties when once set at a temperature which is critical to each resin.

The proportions of thermosetting material to thermoplastic material in the matrix may vary widely depending on a number of factors including whether the matrix material has any ballistic-resistant properties of its own, the rigidity of the thermoplastic and thermosetting resins, and upon the shape, heat resistance, shelf life, wear resistance, flammability resistance and other desired properties desired for the composite article. In general, the higher the proportion of the thermoplastic resin and the lower the proportion of the thermosetting resin in the matrix, the greater the toughness and impact resistance and the longer the shelf life of the composite. However, longer mold cycle times and mold cooling cycles may be required with greater amounts of the thermoplastic resin. Conversely, the lower the proportion of the thermoplastic resin and the higher the proportion of the thermosetting resin in the matrix, the greater the rigidity and the shorter the mold cycle times and mold cooling cycles of the composites. However, toughness and impact resistance of the composite may be decreased relative to those of composites having greater amounts of the thermoplastic resin, and the shelf life of the composites may be decreased relative to those of composites having greater amounts of the thermoplastic resin. Thus, the relative proportions of thermosetting resins and thermoplastic resins are selected to achieve the desired physical properties and process parameters.

The choice of any thermosetting resin and thermoplastic resin for use in the formation of the matrix may vary widely depending on the desired characteristics of the composite. One important characteristic of the matrix material is its modulus which is preferably equal

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to or greater than about 500 psi (3,450 kPa) . The upper limit for the modulus is not critical and usually the higher the modulus the more desirable are composite properties. In the preferred embodiments of the invention, the thermoplastic and thermosetting resins are selected such that the matrix material has a modulus equal to or greater than about 500 psi (3,450 kPa), and in the particularly preferred embodiments, these resins are selected such that the matrix material has a modulus equal to or greater than about 2,000 psi (13,800 kPa). In the most preferred embodiments of the invention, the thermoplastic and thermosetting resins are selected such that the matrix material has a modulus equal to or greater than about 5,000 psi (34,500 kPa).

In general, the amount of thermoplastic resin is from about 10 to about 90 vol% based on total volume of the matrix and the amount of thermosetting resin is from about 90 to about 10 vol% on the aforementioned basis. In the preferred embodiments of the invention the amount of thermoplastic resin is from about 20 to about 80 vol% based on the total volume of the matrix and the amount of thermosetting resin is from about 80 to about 20 vol% on the aforementioned basis. In the particularly preferred embodiments, the amount of thermoplastic resin in the matrix is from about 25 to about 75 vol% based on the volume of matrix and the amount of thermosetting material is from about 75 to about 25 vol% on the aforementioned basis. In the most preferred embodiments of the invention, the amount of thermoplastic resin in the matrix is from about 30 to about 70 vol% based on the total volume of the matrix, and the amount of thermosetting resin in the matrix is from about 70 to about 30 vol% on the aforementioned basis.

Thermosetting resins useful in the practice of this invention may vary widely. Illustrative of useful thermosetting resins are alkyds such as those derived from esterification of polybasic acids, as for example,

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phthalic anhydride, fumaric acid, maleic anhydride, isophthalic acid, terephthalic acid, trimesic acid, hemimellitic acid, succinic anhydride, fatty acids derived from mineral or vegetable oils and the like, and

5 polyhydric alcohols as for example glycerol, ethylene glycol, propylene glycol, pinacol, 1,4-butanediol, 1,3-propanediol, sorbitol, pentaerythritol, 1,2-cyclohexanediol and the like. Other useful thermosetting resins are acrylics such as crosslinkable

10 polyacrylics, polyacrylates, epoxydiacrylates, urethane diacrylates and the like. Still other useful thermosetting resins are amino resins derived from reaction between formaldehyde and various amino compounds such as melamine, urea, aniline, ethylene urea,

15 sulfonamide, dicyanodiamide and the like. Other useful thermosetting resins include urethanes derived from reaction of polyisocyanates or diisocyanates such as 2,6-tolylene diisocyanate, 2,4-tolylene diisocyanate, 4,4'-diphenyl-methane diisocyanate, 4,4'-dicyclohexyl-

20 methane diisocyanate and the like, and polyols such as glycerin, ethylene glycol, diethylene glycol, trimethylolpropane, 1,2,6-hexanetriol, sorbitol, pentaerythritol and the like.

Exemplary of still other thermosetting resins useful

25 in the practice of this invention are unsaturated polyesters derived from reaction of dibasic acids such as maleic anhydride, fumaric acid, adipic acid, azelaic acid and the like, and dihydric alcohols such as ethylene glycol and propylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, diethylene glycol, dipropylene

30 glycols and the like; and silicones such as dimethyldichlorosilane and the like.

Yet another class of useful thermosetting resins are epoxies based on saturated or unsaturated aliphatic, cycloaliphatic, aromatic and heterocyclic epoxides.

35 Useful epoxides include glycidyl ethers derived from epichlorohydrin adducts and polyols, particularly

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polyhydric phenols. Another useful epoxide is the diglycidyl ether of bisphenol A. Additional examples of useful polyepoxides are resorcinol diglycidyl ether, 3,4-epoxy-6-methylcyclohexylmethyl-9,10-epoxystearate, 5 1,2,-bis(2,3-epoxy-2-methylpropoxy)ethane, diglycidyl ether of 2,2-(p-hydroxyphenyl) propane, butadiene dioxide, dicyclopentadiene dioxide, pentaerythritol tetrakis(3,4-epoxycyclohexanecarboxylate), vinylcyclohexene dioxide, divinylbenzene dioxide, 1,5-pentadiol bis(3,4-epoxycyclo- 10 hexane carboxylate), ethylene glycol bis(3,4-epoxycyclohexane carboxylate), 2,2-diethyl-1,3-propanediol bis(3,4-epoxycyclohexanecarboxylate), 1,6-hexanediol bis(3,4-epoxycyclohexanecarboxylate), 2-butene-1,4-diol bis(3,4-epoxy-6-methylcyclohexanecarboxylate), 1,1,1- 15 trimethylolpropane tris (3,4-epoxycyclohexanecarboxylate), 1,2,3-propanetriol tris(3,4-epoxycyclohexanecarboxylate), dipropylene glycol bis(2-ethylexyl-4,5-epoxycyclohexane-1,2-dicarboxylate), diethylene glycol bis(3,4-epoxy-6-methylcyclohexanecarboxylate), triethylene glycol 20 bis(3,4-epoxycyclohexanecarboxylate), 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-1-methylcyclohexylmethyl 3,4-epoxy-1-methylcyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl) pimelate, bis(3,4-epoxy-6-methylenecyclohexylmethyl) maleate, 25 bis(3,4-epoxy-6-methylcyclohexylmethyl) succinate, bis(3,4-epoxycyclohexylmethyl) oxalate, bis(3,4-epoxy-6-methylcyclohexylmethyl) sebacate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, bis(3,4-epoxycyclohexylmethyl) terephthalate, 2,2'-sulfonyldiethanol 30 bis(3,4-epoxycyclohexanecarboxylate), N,N'-ethylene bis(4,5-epoxycyclohexane-1,2-dicarboximide), di(3,4-epoxycyclohexylmethyl) 1,3-tolylenedicarbamate, 3,4-epoxy-6-methylcyclohexanecarboxaldehyde acetal, 3,9-bis(3,4-epoxycyclohexyl) spirobi-(methadioxane), and 35 the like.

Useful thermosetting resins also include phenolic resins produced by the reaction of phenols and aldehydes.



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Useful phenols include phenol, o-cresol, m-cresol, p-cresol, p-tertbutylphenol, p-tertoctylphenol, p-nonylphenol, 2,3-xyleneol, 2,4-xyleneol, 2,5-xyleneol, 2,6-xyleneol, 3,1-xyleneol, 3,4-xyleneol, resorcinol, 5 bisphenol-A and the like. Useful aldehydes include formaldehyde, acetoldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, glyoxal, furfural and the like.

Other useful thermosetting resins are aromatic 10 vinylesters such as the condensation product of epoxide resins and unsaturated acids usually diluted in a compound having double bond unsaturation such as vinylaromatic monomer as for example styrene and vinyltoluene, and diallyl phthalate. Illustrative of useful vinylesters are 15 diglycidyl adipate, diglycidyl isophthalate, di(2,3-epoxybutyl) adipate, di(2,3-epoxybutyl) oxalate, di(2,3-epoxyhexyl) succinate, d(3,4-epoxybutyl) maleate, d(2,3-epoxyoctyl) pimelate, di(2,3-epoxybutyl) phthalate, di(2,3-epoxyoctyl) tetrahydrophthalate, di(4,5-epoxy- 20 dodecyl) maleate, di(2,3-epoxybutyl) terephthalate, di(2,3-epoxypentyl) thiodipropionate, di(5,6-epoxy-tetradecyl) diphenyldicarboxylate, di(3,4-epoxyheptyl) sulphonyldibutyrate, tri(2,3-epoxybutyl) 1,2,4 butanetricarboxylate, di(5,6-epoxypentadecyl) maleate, 25 di(2,3-epoxybutyl) azelate, di(3,4-epoxybutyl) citrate, di(5,6-epoxyoctyl) cyclohexane-1,3-dicarboxylate, di(4,5-epoxyoctadecyl) malonate, bisphenol-A-fumaric acid polyester and the like.

Preferred thermosetting resins for use in the 30 practice of this invention are vinyl esters, unsaturated polyesters, epoxies and phenolics.

Particularly preferred thermosetting resins are vinyl esters, epoxies and phenolics, with vinylesters being the thermosetting resin of choice.

35 Thermoplastic resins for use in the practice of this invention may also vary widely. Illustrative of useful thermoplastic resins are polylactones such as

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poly(pivalolactone), poly(ε-caprolactone) and the like; polyurethanes derived from reaction of diisocyanates such as 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, dianisidine diisocyanate, tolidine diisocyanate, hexamethylene diisocyanate, 4,4'-diisocyananodiphenylmethane and the like and linear long-chain diols such as poly(tetramethylene adipate), poly(ethylene adipate), poly(1,4-butylene adipate), poly(1,5-pentylene adipate), poly(1,3 butylene adipate), poly(ethylene succinate), poly(2,3-butylene succinate), polyether diols and the like; polycarbonates such as poly[methane bis (4-phenyl) carbonate], poly[1,1-ether bis(4-phenyl) carbonate], poly[diphenylmethane bis (4-phenyl)carbonate], poly[1,1-cyclohexane bis(4-phenyl)carbonate] and the like; poly sulfones; polyether ether ketones; polyamides such as poly(4-amino butyric acid), poly(hexamethylene adipamide), poly(6-aminohexanoic acid), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(metaphenyleneisophthalamide) (Nomex), poly(p-phenylene terephthalamide) (Kevlar), and the like; polyesters such as poly(ethylene azelate), poly(ethylene-1,5-naphthalate), poly(1,4-cyclohexane dimethylene terephthalate), poly(ethylene oxybenzoate) (A-Tell), poly(para-hydroxy benzoate) (Ekonol), poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel)(as), poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel) (trans), polyethylene terephthalate, polybutylene terephthalate and the like; poly(arylene oxides) such as poly(2,6-dimethyl-1,4-phenylene oxide), poly(2,6-diphenyl-1,4-phenylene oxide)

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and the like; poly(arylene sulfides) such as poly(phenylene sulfide) and the like; polyetherimides; thermoplastic elastomers such as polyurethane elastomers, fluoroelastomers, butadiene/acrylonitrile elastomers, 5 silicone elastomers, polybutadiene; polyisobutylene, ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, polychloroprene, polysulfide elastomers, block copolymers, made up of segments of glassy or crystalline blocks such as polystyrene, poly(vinyl- 10 toluene), poly(t-butyl styrene), polyester and the like and the elastomeric blocks such as polybutadiene, polyisoprene, ethylene-propylene copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in polystyrene- 15 polybutadiene-polystyrene block copolymer manufactured by Shell Chemical Company under the trade name of Kraton ; vinyl polymers and their copolymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl butyral, polyvinyl- 20 idene chloride, ethylene-vinyl acetate copolymers, and the like; polyacrylics, polyacrylate and their copolymers such as polyethyl acrylate, poly(n-butyl acrylate), polymethyl methacrylate, polyethyl methacrylate, poly(n-butyl methacrylate), poly(n-propyl methacrylate), polyacryl- 25 amide, polyacrylonitrile, polyacrylic acid, ethylene-acrylic acid copolymers, methyl methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylated budadiene-styrene copolymers and the like; polyolefins such as low density polyethylene, 30 polypropylene, chlorinated low density polyethylene, poly(4-methyl-1-pentene) and the like; ionomers; and polyepichlorohydrins.

In the preferred embodiments of the invention, the thermoplastic material is selected from the group 35 consisting of polyurethanes, polyvinyls, polystyrene-polyisoprene-polystyrene block copolymer thermoplastic elastomers, polyacrylics and polyolefins. In the

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particularly preferred embodiments of the invention the preferred thermoplastic material is a polyurethane.

The proportions of matrix to filament in the composite is not critical and may vary widely depending on a number of factors including, whether the matrix material has any ballistic-resistant properties of its own (which is generally not the case) and upon the rigidity, shape, heat resistance, wear resistance, flammability resistance mold cycle time, handling characteristics and other properties desired for the composite article. In general, the proportion of matrix to filament in the composite may vary from relatively small amounts where the amount of matrix is about 10% by volume of the filaments to relatively large amounts where the amount of matrix is up to about 90% by volume of the filaments. In the preferred embodiments of this invention, matrix amounts of from about 15 to about 85% by volume are employed. All volume percents are based on the total volume of the composite. In the particularly preferred embodiments of the invention, ballistic-resistant articles of the present invention contain a relatively minor proportion of the matrix (e.g., about 10 to about 30% by volume of composite), since the ballistic-resistant properties are almost entirely attributable to the filament, and in the particularly preferred embodiments of the invention, the proportion of the matrix in the composite is from about 10 to about 30% by volume of filaments.

The articles of this invention can be fabricated using a number of procedures. In general, the layers are formed by molding the combination of the matrix material and filaments in the desired configurations and amounts by subjecting the combination to heat, and pressure during a mold cycle time. An advantage of those embodiments of this invention in which the thermosetting resin is a vinyl ester is that relative short mold cycle times and temperatures may be employed.

The filaments may be premolded by subjecting them to

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heat and pressure. For example, for extended chain polyethylene filaments, molding temperatures range from about 20 to about 150°C, preferably from about 80 to about 145°C, more preferably from about 100 to about 135°C depending on the type of matrix material selected. The molding pressure may range from about 10 psi (69 kPa) to about 10,000 psi (69,000 kPa). A pressure between about 10 psi (69 kPa) and about 100 psi (690 kPa), when combined with temperatures below about 100°C for a period of time less than about 1.0 min., may be used simply to cause adjacent filaments to stick together. Pressures from about 100 psi to about 10,000 psi (69,000 kPa), when coupled with temperatures in the range of about 100 to about 155°C for a time of between about 1 to about 5 min., may cause the filaments to deform and to compress together (generally in a film-like shape). Pressures from about 100 psi (690 kPa) to about 10,000 psi (69,000 kPa), when coupled with temperatures in the range of about 150 to about 155°C for a time of between 1 to about 5 min., may cause the film to become translucent or transparent. For polypropylene filaments, the upper limitation of the temperature range would be about 10 to about 20°C higher than for ECPE filament.

In the preferred embodiments of the invention, the filaments (premolded if desired) are precoated with the desired matrix material prior to being arranged in a network and molded as described above. The coating may be applied to the filaments in a variety of ways and any method known to those of skill in the art for coating filaments may be used. For example, one method is to apply the matrix material to the stretched high modulus filaments either as a liquid, a sticky solid or particles in suspension, or as a fluidized bed. Alternately, the matrix material may be applied as a solution or emulsion in a suitable solvent which does not adversely affect the properties of the filament at the temperature of application. In these illustrative embodiments, any

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liquid capable of dissolving or dispersing the matrix material may be used. However, in the preferred embodiments of the invention useful solvents include water, paraffin oils, ketones, alcohols, aromatic solvents  
5 or hydrocarbon solvents or mixtures thereof, with illustrative specific solvents including paraffin oil, xylene, toluene and octane. The techniques used to dissolve or disperse the matrix in the solvents will be those conventionally used for the coating of thermoplastic  
10 resins on a variety of substrates.

Other techniques for applying the coating to the filaments may be used, including coating of the high modulus precursor (gel filament) before the high temperature stretching operation, either before or after  
15 removal of the solvent from the filament. The filament may then be stretched at elevated temperatures to produce the coated filaments. The gel filament may be passed through a solution of the appropriate matrix material, as for example an elastomeric material dissolved in paraffin  
20 oil, or an aromatic or aliphatic solvent, under conditions to attain the desired coating. Crystallization of the polymer in the gel filament may or may not have taken place before the filament passes into the cooling solution. Alternately, the filament may be extruded into  
25 a fluidized bed of the appropriate matrix material in powder form.

The proportion of coating on the coated filaments or fabrics may vary from relatively small amounts (e.g., 1% by weight of filaments) to relatively large amounts (e.g.,  
30 150% by weight of filaments), depending upon whether the coating material has any impact or ballistic-resistant properties of its own (which is generally not the case) and upon the rigidity, shape, heat resistance, wear resistance, flammability resistance and other properties  
35 desired for the complex composite article. In general, ballistic-resistant articles of the present invention containing coated filaments should have a relatively minor

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proportion of coating (e.g., about 10 to about 30 percent by volume of filaments), since the ballistic-resistant properties are almost entirely attributable to the filament. Nevertheless, coated filaments with higher  
5 coating contents may be employed. Generally, however, when the coating constitutes greater than about 60% (by volume of filament), the coated filament is consolidated with similar coated filaments to form a simple composite without the use of additional matrix material.

10 Furthermore, if the filament achieves its final properties only after a stretching operation or other manipulative process, e.g. solvent exchanging, drying or the like, it is contemplated that the coating may be applied to a precursor material of the final filament. In  
15 such cases, the desired and preferred tenacity, modulus and other properties of the filament should be judged by continuing the manipulative process on the filament precursor in a manner corresponding to that employed on the coated filament precursor. Thus, for example, if the  
20 coating is applied to the xerogel filament described in U.S. Application Ser. No. 572,607 of Kavesh et al., and the coated xerogel filament is then stretched under defined temperature and stretch ratio conditions, then the filament tenacity and filament modulus values would be  
25 measured on uncoated xerogel filament which is similarly stretched.

It is a preferred aspect of the invention that each filament be substantially coated with the matrix material for the production of composites having improved impact  
30 protection, delamination resistance, rigidity and/or ballistic resistance, and relatively shorter mold cycle times, preferably of less than about 30 minutes. A filament is substantially coated by using any of the coating processes described above or can be substantially  
35 coated by employing any other process capable of producing a filament coated essentially to the same degree as a filament coated by the processes described heretofore

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(e.g., by employing known high pressure molding techniques).

The filaments and networks produced therefrom are formed into "simple composites" as the precursor to preparing the complex composite articles of the present invention. The term, "simple composite", as used herein is intended to mean composites made up of one or more layers, each of the layers containing filaments as described above with a single major matrix material, which material may include minor proportions of other materials such as fillers, lubricants or the like.

The proportion of matrix material to filament is variable for the simple composites, with matrix material amounts of from about 5% to about 150 vol%, by volume of the composite, representing the broad general range. Within this range, it is preferred to use composites having a relatively high filament content, such as composites having only about 10 to about 30 vol% matrix material by volume of the composite.

Stated another way, the filament network occupies different proportions of the total volume of the simple composite. Preferably, however, the filament network comprises at least about 30 volume percent of the simple composite. For ballistic protecting, the filament network comprises at least about 50 volume percent, more preferably about 70 volume percent, and most preferably at least about 75 volume percent, with the matrix occupying the remaining volume.

A particularly effective technique for preparing a preferred composite of this invention comprised of substantially parallel, unidirectional aligned filaments includes the steps of pulling a filament or bundles of filaments through a bath containing a solution of a matrix material and circumferentially winding this filament into a single sheet-like layer around and along a bundle of filaments the length of a suitable form, such as a cylinder. The solvent, if used, is then evaporated



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leaving a sheet-like layer of filaments embedded in a matrix that can be removed from the cylindrical form. Alternatively, a plurality of filaments or bundles of filaments can be simultaneously pulled through the bath  
5 containing a solution or dispersion of a matrix material and laid down in closely positioned, substantially parallel relation to one another on a suitable surface. Evaporation of the solvent leaves a sheet-like layer comprised of uni-directional filaments which are coated  
10 with the matrix material and which are substantially parallel and aligned along a common filament direction. The sheet is suitable for subsequent processing such as laminating to another sheet to form composites containing more than one layer.

15 Similarly, a filament-type simple composite can be produced by pulling a group of filament bundles through a dispersion or solution of the matrix material to substantially coat each of the individual filaments, and then evaporating the solvent to form the coated yarn. The  
20 yarn can then, for example, be employed to form fabrics, which in turn, can be used to form more complex composite structures. Moreover, the coated yarn can also be processed into a simple composite by employing conventional filament winding techniques; for example, the  
25 simple composite can have coated yarn formed into overlapping filament layers.

The number of layers included in the composite of this invention may vary widely depending on the uses of the composite, for example, in those uses where the  
30 composite would be used as ballistic protection, the number of layers would depend on a number of factors including the degree of ballistic protection desired and other factors known to those of skill in the ballistic protection art. In general for this application, the  
35 greater the degree of protection desired the greater the number of layers included in the article for a given weight of the article. Conversely, the lesser the degree

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of ballistic protection required, the lessor the number of layers required for a given weight of the article. It is convenient to characterize the geometries of such composites by the geometries of the filaments and then to indicate that the matrix material may occupy part or all of the void space left by the network of filaments. One such suitable arrangement is a plurality of layers or laminates in which the coated filaments are arranged in a sheet-like array and aligned parallel to one another along a common filament direction. Successive layers of such coated, uni-directional filaments can be rotated with respect to the previous layer. An example of such laminate structures are composites with the second, third, fourth and fifth layers rotated  $+45^\circ$ ,  $-45^\circ$ ,  $90^\circ$  and  $0^\circ$ , with respect to the first layer, but not necessarily in that order. Other examples include composites with  $0^\circ/90^\circ$  layout of yarn or filaments.

One technique for forming composites of this invention having more than one layer includes the steps of arranging coated filaments into a desired network structure, and then consolidating and heat setting the overall structure to cause the coating material to flow and occupy the remaining void spaces, thus producing either a continuous or a discontinuous matrix without a mold cooling cycle or with a relatively short mold cooling cycle. Another technique is to arrange layers or other structures of coated or uncoated filament adjacent to and between various forms, e.g. fabric films, of the matrix material and then to consolidate and heat set the overall structure. In the above cases, it is possible that the matrix can be caused to stick or flow without completely melting. In general, if the matrix material is caused to melt, relatively little pressure is required to form the composite; while if the matrix material is only heated to a sticking point, generally more pressure is required. Also, the pressure and time to set the composite and to achieve optimal properties will generally depend on the

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nature of the matrix material (chemical composition as well as molecular weight) and processing temperature.

The composites of this invention comprising one or more layers may be incorporated into complex composites.

5 For example, such composites may be incorporated into more complex composites to provide a more rigid complex composite article suitable, for example, as structural ballistic-resistant components, such as helmets, structural members of aircraft, and vehicle panels. The  
10 term "rigid" as used in the present specification and claims, is intended to include semi-flexible and semi-rigid structures that are capable of being free standing, without collapsing. To form the complex composite, at least one substantially rigid layer is  
15 bonded or otherwise connected to a major surface of the mono or multi-layer composite. The resultant complex composite article is capable of standing by itself and is impact and delamination resistant. Where there is only one layer, the composite of this invention ordinarily  
20 forms a remote portion of the complex composite article; that is a portion that is not initially exposed to the environment, e.g., the impact of an oncoming projectile. Where there is more than one layer, the simple composite may form, for example, a core portion that is sandwiched  
25 between two or more rigid layers, as is particularly useful, for example, in helmet applications. Other forms of the complex composite are also suitable, for example a composite comprising multiple alternating layers of simple composite and rigid layer.

30 In the preferred embodiments of the invention, rigid layers are preferably comprised of an impact resistant material, such as steel plate, composite armor plate, ceramic reinforced metallic composite, ceramic plate, concrete, and high strength filament composites (for  
35 example, an aramid, polyethylene or glass filament and a high modulus, resin matrix such as an epoxy resin, a phenolic resin, a vinyl ester resin, an unsaturated

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polyester, nylon 6, nylon 6,6 and polyvinylidene halide). Most preferably, the rigid impact resistant layer is one which is ballistically effective, such as ceramic plates or ceramic reinforced metal composites. A desirable  
5 embodiment of our invention is the use of a rigid impact resistant layer which will at least partially deform the initial impact surface of the projectile or cause the projectile to shatter such as aluminum oxide, boron carbide, silicon carbide and beryllium oxide (see Laible,  
10 supra, Chapters 5-7 for additional useful rigid layers). For example, a particularly useful ballistic resistant complex composite comprises a simple composite comprising highly-oriented high molecular weight polyethylene filament in a matrix on which is formed at least one layer  
15 comprising a material which may be heat resistant, flame resistant, solvent resistant, radiation resistant, or combinations thereof such as stainless steel, copper, aluminum oxides, titanium, titanium boride and the like.

A portion of the rigid impact resistant composite,  
20 the volume percent of the simple composite is variable depending upon the desired properties of the final product. The volume percent of the simple composite to the complex composite is ordinarily at least about 10%, preferably at least about 15%, and most preferably at  
25 least 20% (for maximizing ballistic resistance). The volume percent of the simple composite to the complex composite is ordinarily at least about 5%, preferably at least about 10%, and most preferably at least about 15% (for maximizing ballistic resistance). The examples  
30 illustrate the effectiveness of a simple composite in a complex structure at various percentages of the simple composite to the total. For example, various compromises between structural rigidity and ballistic performance are attainable depending upon the specific material choices  
35 and the relative properties of the simple composites and rigid layers.

The multilayer composites of this invention exhibits

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enhanced peel strength as compared to conventional multilayer composites which results in reduced delamination of the composite on impact. In the preferred embodiments of the invention, peel strength between at least two adjacent layers of the multilayer composite is at least about 1.5 lbs/in as determined by the peel resistance test of ASTM-D-1876-72, and in the more preferred embodiments of the invention, the peel strength between at least two adjacent layers of the composite is equal to or greater than about 3 lbs/in. In the most preferred embodiments of the invention, the peel strength between at least two adjacent layers of the composite is equal to or greater than about 6 lbs/in, with those multilayer composites having layer peel strength equal to or greater than about 8 lbs/in being the composites of choice.

The composites of this invention can be used for conventional purposes. For example, such composites can be used in the fabrication of structural parts, ballistic armor and the like using conventional methods.

The following examples are presented to provide a more complete understanding of the invention and are not to be construed as limitations thereon. In the examples, the following technical terms are used:

(a) "Areal Density" which is the weight of the armor material per unit area usually in  $\text{Kg/m}^2$  or  $\text{lb/ft}^2$ .

(b) " $V_{50}$ " which is the projectile velocity which is statistically at the borderline penetration and partial penetrations which has a 50% probability of penetrating the target. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles of the invention are exemplary and should not be construed as limiting the scope of the invention.

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EXAMPLE I

This example illustrates the advantages of using a homogeneous blend of a thermoplastic polyurethane and a thermoset vinyl/ester as the matrix-resin system. The resin system is formulated as shown in the following Table I.

Table I

Components	weight (g)	solids, weight (g)
1 Derekane 8084(a)	60	30
2 Diallyl phthalate monomer	12	12
3 Lupersol 256(b)	0.36	0.36
4 Dispercoll E585(c)	175	70

(a) "Derekane 8084" is an aqueous dispersion of vinyl ester/styrene monomer (50/50 wt/wt) manufactured and sold by Dow Chemical Company.

(b) "Lupersol 256" is 2,5-dimethyl-2,5-di-2-ethylhexanoylperoxyhexane manufactured and sold by Penwalt Corporation.

(c) "Dispercoll E585" is an aqueous dispersion of a thermoplastic polyurethane manufactured and sold by Mobay Corporation.

The above resin components were homogeneously mixed within a container. Water was then added to achieve the proper viscosity level suitable for coating the filaments. The weight ratio between thermoplastic polyurethane (Dispercoll E585), and thermoset vinyl ester (calculated based on the solid content basis) was 70/30. Using this resin and Spectra -1000 yarns of 650 deniers/118 filaments, uniaxial prepreg tapes were produced. The prepreg tapes (12 inch (30.4 cm) x 0.0025 inch (0.0064 cm) contained approximately 75% weight fibers and 25% weight resin. The prepreg tapes were cut into 12"

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(30.4 cm) x 12" (30.4 cm) layers which were subsequently stacked into 0°, 90° yarn orientation between adjacent layers. A panel consisting of 132 layers was molded under pressure of approximately 400 psi (2758 kPa) at a temperature of 115°C for a mold cycle time of 20 minutes. The molded panel was then removed from the mold at 115°C without any mold cooling. The panel surface appeared flat without any visual distortion.

The molded panel is rigid and had an areal density of 1.42 lbs./ft<sup>2</sup> (6.9 Kg/m<sup>2</sup>) and a V<sub>50</sub> of 2,206 ft/sec (673 m/sec) against fragment simulators.

The flexural properties of the panels under 72°F (22°C), 160°F (71°C) for 72 hours and -60°F (-45°C) for 72 hours were determined using the procedure of ASTM-D-790. The results are summarized in the following Table II.

Table II

Environmental Treatment	Stress at 5% Flexural	
	Strain psi (kPa)	Modulus psi (KPa)
1 72°F (22°C) 947,000 (6.5 x 10 <sup>6</sup> )	4,510 (31,100)	
2 160°F (71°C) 72 hrs. oven, hot air 1,190,000 (8.2 x 10 <sup>6</sup> )	5,030 (34,700)	
3 -90°F (-68°C) 72 hrs. freezer 896,000 (6.2 x 10 <sup>6</sup> )	4,050 (27,900)	

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EXAMPLE II

Example 1 was repeated except that the ratio of polyurethane to vinyl ester based on solid content was 40/60. Uniaxial prepreg tapes made with the 40/60 composition were difficult to handle because of the stickiness during cut and stack sequence.

EXAMPLE III

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Example 1 was repeated except that the ratio of polyurethane/vinyl ester was 90/10. Uniaxial prepreg tapes were easily cut and stacked into 12" (30.4 cm) x 12" (30.4 cm) layers. The molded panels were, however, very soft and severe deformation was observed when removed from the mold at a temperature of 115°C which was above the solidification temperature of polyurethane. However, the molded panels were removed easily without any visual distortion if the mold was cooled down from 115°C to room temperature of 23°C. The panel had an areal density of 1.3 lbs/ft<sup>2</sup> (6.3 Kg/cm<sup>2</sup>). The ballistic V<sub>50</sub> performance was 2,316 ft/sec (706 m/sec).

EXAMPLE IV

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Example I was repeated except that Spectra -1000 fabric was impregnated with a blend of polyurethane/vinyl ester in a 70/30 ratio. The fabrics/prepreg consisted of about 25% resin and 75% Spectra - 1000 fabric. A panel (12" (30.4 cm) x 12" (30.4 cm)) was molded from 20 layers of fabric prepreg at a temperature of 115°C and a pressure of 400 psi (2,760 kPa) for 20 minutes without mold cooling cycle. The panel was then cut into 1" (2.54 cm) x 12" (30.4 cm) strips. The peel resistance test, or T-peel test, was carried out according to the standard method outlined in ASTM-D-1876-72. At an Instron speed of 0.2" (0.5 cm) per minute, the peel strength was 5 lbs. per



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linear inch (0.89 kg/cm) which is far stronger than 1.5  
lbs. per linear inch for strips molded from fabrics  
impregnated with vinyl ester resin under otherwise  
identical conditions. Higher peel strength represents  
5 higher interfacial adhesion which resists delamination  
upon impact.

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WHAT IS CLAIMED IS:

1. An impact resistance composite comprised of one or more layers; at least one of said layers is a fibrous layer comprising a network of fibers having a tensile modulus of at least about 150 g/denier, and an energy-to-break of at least about 8 j/g and a tenacity  
5 equal to or greater than about 7 g/denier in a rigid matrix wherein said matrix comprises one or more thermosetting resins and one or more thermoplastic resins.
2. A composite as recited in claim 1 wherein said  
10 composite comprises more than one layer and wherein the peel strength between at least two adjacent layers is equal to or greater than about 1.5 lbs/in.
3. A composite as recited in claim 2 wherein said  
15 peel strength is equal to or greater than about 3 lbs/in.
4. A composite as recited in claim 3 wherein said  
peel strength is equal to or greater than about 6 lbs/in.
5. A composite as recited in claim 4 wherein said  
20 peel strength is equal to or greater than about 8 lbs/in.
6. A composite as recited in claim 1 wherein said network of fibers comprises a sheet-like fiber array in which said fibers are arranged substantially  
25 parallel to one another along a common fiber direction.
7. A composite as recited in claim 6 wherein said composite comprises more than one layer, with adjacent layers aligned at an angle with respect to the common fiber direction of the parallel fibers  
30 contained in said layers.
8. A composite as recited in claim 1 wherein said matrix material comprises one or more thermosetting resins selected from the group consisting of vinyl esters, phenolics, epoxies, allylics, urethanes,  
35 unsaturated polyesters and alkyds, and one or more

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thermoplastic resins selected from the group consisting of polyamides, polystyrene-polyisoprene-polystyrene block copolymers, polyacrylics, polycarbonates, polyurethanes, 5 polyarylene oxides, polyarylene sulfones, polyarylene sulfides, polyacetals, polyvinyl acetates, polyether ether ketones, polyaramids, polyesteramides, and polyimides.

9. A composite as recited in claim 1 wherein said 10 matrix material comprises a thermoplastic polyurethane and a thermosetting vinyl ester resin.

10. A composite as recited in claim 1 wherein said fibers are selected from the group consisting of polyethylene fibers, aramid fibers and a combination 15 thereof.